# A STUDY OF THE BLISTERING OF METAL SURFACES BY SOLAR SYSTEM IONS

August, 1966



FINAL REPORT

Contract NASw-1203

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## ABSTRACT

Samples of pure aluminum, pure gold, and vapor deposited gold on aluminum were irradiated with protons. Tests with pure gold were inconclusive because of rough sample surfaces. Spontaneous blistering and gold removal occurred on the vapor deposited samples during irradiation with 10 and 30 Kev protons. Some oxide removal and blistering during irradiation also occur on pure aluminum samples for protons of less than 100 Kev energy. Pure aluminum irradiated with 100 Kev protons blisters only after annealing at 250°C or higher. The blisters have been shown to occur in the aluminum rather than in the oxide. Pitting occurs in the aluminum oxide during irradiation and the areal pit density has been correlated with crystallographic orientation of the aluminum. Possibility of a similar correlation for the blisters is being studied.

## FOREWORD

This report was prepared by the Avco Instrument Division and the Oklahoma University Research Institute as the final documentation of work performed under Contract NASw-1203, issued by the Headquarters Office of the National Aeronautics and Space Administration. This program was monitored by Dr. R. R. Nash of NASA-Headquarters and D. L. Anderson of NASA/Ames.

This report covers work performed from May, ~~1965 through May,~~ 1966. A follow-on contract (NASw-1431) has been initiated covering the continuation of this work from June, 1966 through June, 1967.

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# I. INTRODUCTION

This is the final report prepared under Contract No. NASw-1203 for a "Study of Radiation Induced Blistering of Metal Surfaces by Solar System Ions." The program is a continuation of the study begun under Contract No. NASw-920 in 1964. The study was funded through the NASA Office of Advanced Research and Technology with Dr. R. R. Nash as technical monitor. Additional technical guidance was obtained from Mr. D. L. Anderson of NASA/Ames.

The Program has been a joint venture of the Avco Instrument Division and the College of Engineering of the University of Oklahoma. The study is being continued for another year under Contract NASw-1431.

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## II. BACKGROUND

In 1963, in the course of studying the discoloration of aluminum samples subjected to proton radiation in the 100 Kev energy range under high vacuum, it was noted that the surface of the metal, in addition to being discolored, contained numerous surface eruptions which were identified as blisters. Because the blistering phenomenon occurred on aluminum, a material used for various optical surfaces on spacecraft, and resulted from particle radiation of a type and energy to be found in space environments, the observation was of considerable practical importance as well as theoretical interest.

A few additional experiments showed the reproducibility of the blistering phenomenon and demonstrated, on 6061-T6 aluminum alloy sheet irradiated with $10^{17}$ protons/$cm^2$ at 200 Kev, that the surface did not blister during the irradiation, but that blistering occurred during subsequent annealing in the temperature range of 250 - 350$^{\circ}$C. These experiments also indicated that the size, shape, and density of surface blisters obtained were sensitive to the processing history and the surface preparation of the aluminum samples.

At about this same time, results of studies of the agglomeration of hydrogen in aluminum and beryllium introduced by irradiation with 7 Mev protons appeared in the literature[1,2]. Although these investigations were concerned with evaluation of hydrogen agglomerations within the bulk material, because of the greater proton penetrations involved, the manner of proton penetration and the hydrogen behavior determined in these investigations was useful as a guide to analysis and interpretation of the blistering phenomenon observed at lower proton energies.

The present research program was initiated under NASA support in 1964 for the purpose of analyzing the processes which cause blistering in proton irradiated metals[3].

Soon after the research program was initiated, it was learned that other investigators, concerned with the optical and thermal properties of spacecraft surface materials, had encountered the phenomenon of blistering of vapor deposited gold and aluminum coatings and of polished aluminum surfaces subjected to proton radiation in the energy range 1 to 10 Kev[4,5]. It was reported that blistering occurred during irradiation without the necessity of post-irradiation annealing. These results further emphasized the need for a detailed study of the problem and suggested that the blistering phenomenon may be the observable result of some rather complex interactions involving the structure and surface characteristics of materials and the radiation parameters.

The problem of hydrogen blistering of aluminum and its alloys predates the specific problem of hydrogen pickup through proton irradiation in outer space environments by many years. The problem of formation of internal bubbles and surface blisters has been of concern to aluminum fabricators since the birth of the industry. The processes generally responsible for excess hydrogen in aluminum are retention in the solid of hydrogen dissolved in the liquid phase and the absorption in the solid of hydrogen produced at the surface in corrosion reactions[6,7]. Although improved industrial practice has overcome many of the difficulties encountered with hydrogen in commercial aluminum alloys, there is continuing interest in the subject because of the potential for hydrogen pickup in the various phases of fabrication of aluminum and because a detailed knowledge of the processes involved is still lacking.

The aim of the present work is to specify the conditions under which hydrogen in aluminum, introduced by proton irradiation, will produce surface blistering and to ascertain the mechanisms of the processes involved and the dependence of the phenomenon on material structure and preparation procedures.

Basic parameters which may play an important role in the blistering process are the penetration depth and distribution of protons in aluminum, the solubility of hydrogen in aluminum, the mobility of hydrogen in aluminum, and the effects of lattice defects, impurities, and the oxide surface film on the distribution and transport of hydrogen in aluminum. Theoretical questions involved are the mechanisms of transport of hydrogen in the metal and evolution of this gas from the metal, the role of lattice defects, impurities and the oxide surface film in the transport and evolution processes, and the mechanism of blister formation.

## III. EXPERIMENTAL APPROACH AND TECHNIQUES

The experimental approach used in this investigation centers on the fact that observable surface blistering can be produced in aluminum under appropriate conditions of irradiation and thermal treatment of the metal, and that these conditions are sensitive to certain basic microstructural characteristics of the metal itself. The primary tool of analysis has been optical metallography. Techniques of electron metallography are being developed to supplement the optical techniques. These techniques make it possible to qualitatively describe the blister phenomenon and its relationship to microstructural features of aluminum. Annealing treatments used to promote blistering provide additional information on the influence of microstructure on blister formation and help to establish the growth kinetics of the microscopically observed blisters.

The necessary conditions for blister formation and the characteristics of the blister patterns developed have been studied as a function of the radiation parameters and the properties and preparation of the material being irradiated. The radiation parameters under study are proton energy, flux density, total or integrated flux, and sample temperature during irradiation. Except for some preliminary experiments, the work to date involving radiation parameters has been concerned primarily with the effects of proton energy on the blister phenomenon. Substrate temperature has been held to $70^{\circ}F$, the total flux has been $10^{17}$ protons/$cm^2$ and the flux density has been either $11 \times 10^{12}$ p/$cm^2$/sec or $1.5 \times 10^{12}$ p/$cm^2$/sec. These values of flux density were dictated on the one hand by the desire to minimize the time required to obtain $10^{17}$ p/$cm^2$ and, on the other hand by limitations on the flux density obtainable with the accelerator when used to obtain lower energy protons. Proton energies were varied between 200 Kev and 7 Kev[3]. Sample irradiations performed during the present contract year are listed in the Appendix.

The material employed, except for some auxiliary experiments on gold and vacuum evaporated gold films, has been aluminum, spectroscopically analyzed as being of 99.997+ % purity. The impurities present are iron 0.001% and magnesium 0.001%. All other possible impurities are below the limit of reliable analysis.

From a theoretical point of view, the ideal material with which to work would be a defect-free, impurity-free, single crystal aluminum without an oxide film. The behavior of the material in this initial condition could be evaluated under proton irradiation for various crystallographic orientations of the surface, and the results obtained could then be compared with results obtained with controlled additions of impurities and defects and with the presence of a surface oxide film. From a practical point of view it is impossible to achieve the above conditions. Single crystals can be prepared, but they are neither defect-free nor impurity-free and, although it is possible under ultra-high vacuum conditions to prepare film-free aluminum, this technique has not been exploited as yet.

The approach thus far has been to evaluate the blistering phenomenon in aluminum crystals of relatively high purity under conditions where the defect structure and characteristics of the surface film are known and, to an extent, can be controlled. These samples have been, for the most part, single crystals or extremely large-grain polycrystals on which the irradiated area is confined to a few grains which can be treated individually like single crystals.

The sample types and preparation procedures employed can be classified as follows:

A. Wrought Samples

1. Fine grained material prepared by recrystallization of swaged samples cut from a cast ingot.

2. Large grained material prepared by recrystallization of swaged samples coupled with a long time grain growth anneal.

B. Remelted Samples

1. Single crystals prepared by remelting and directional solidification in a Bridgeman type furnace.

2. Samples prepared in the Bridgeman furnace as described above, but containing two or three large grains running parallel to the direction of solidification.

Polycrystalline samples prepared by recrystallization of high purity aluminum have been utilized for two reasons: first, to compare blistering behavior in high purity polycrystals with that in wrought alloy samples and, second, as a method for preparing large crystals by a technique which avoids subgrain structures which develop during growth from the melt.

Single crystals have been prepared by the Bridgman technique in a graphite crucible under an argon atmosphere. Unseeded crystals all show a preferred growth direction of high indices. The average growth direction is approximately $34^{\circ}$ from (100), $22^{\circ}$ from (110), and $30^{\circ}$ from (111) on a stereographic net. Attempts to seed low indices growth directions have been only partially successful in that the growth direction could be warped only about 15 degrees toward a major axis from the preferred high indices growth direction.

Most single crystal samples grown from the melt have contained observable substructures. The substructures are of two general types which can be denoted as cellular and lamellar[8]. Subgrain boundaries are believed to form as a consequence of impurities in the melt which give rise to constitutional supercooling. Microsegregation then occurs with the impurities concentrated at the subgrain boundaries.

Most studies of microsegregation have been conducted with impurities as chosen additives in purer metals, suggesting that the aluminum under study must be of lower purity than our analyses indicated or that impurities were being introduced in the melt process. A recent study of impurity segregation by electron microprobe analysis, however, demonstrates that the impurity level necessary for substructure formation is well within the impurity level of 99.997+ aluminum[9]. The study further indicates that the concentration enhancements in the regions of microsegregation can be as much as two orders of magnitude.

The surfaces of aluminum samples used in the irradiation studies have been prepared by electropolishing. The samples were polished in a 2:1 methyl alcohol-nitric acid solution followed by rinsing in an 85% orthophosphoric, 3.5% nitric acid solution. Technique in the electropolishing process was critical in obtaining reproducible results. Solution temperature, current density, and polishing time have been found to be important factors in the process.

A tendency for pitting to occur in the electropolishing process, particularly on crystals grown from the melt by the Bridgeman technique, has been linked with the substructure of the aluminum. The pitting tended to be localized along boundaries which subsequent irradiation and annealing revealed to be regions of high

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blister content. These regions are believed to be subgrain boundaries formed during solidification, and the preferential etching response was to be expected. Attempts to eliminate this preferential etching by modification of the polishing procedure have been partially successful. The important thing is to keep the time short.

Although electropolishing techniques have been designed to substantially reduce pitting in samples being prepared for irradiation, the intentional development of pitting in grown crystals appears to be a useful technique for identifying substructures.

The thicknesses of the oxide films formed on the aluminum samples in the preparation process have been determined by the technique developed by Hunter, Fowle, and Towner[10, 11]. The technique is based upon a combination of the characteristics of barrier layer type anodic coatings and interference color methods. The barrier layer has been found to be about ten angstroms and the total thickness of the oxide, including the porous layer, about 60 angstroms for the electropolished surfaces.

In addition to the radiation experiments on aluminum crystals, studies have been initiated on samples of gold and on vapor deposited gold coatings on aluminum substrates. These studies have been initiated to complement the work on aluminum using a material on which there is no oxide layer, and are an attempt to reproduce and interpret results reported elsewhere on the gold films[4].

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## IV. DISCUSSION OF RESULTS

Results obtained thus far in the investigation make possible a reasonably consistent qualitative description of the proton irradiation induced blistering process in aluminum. The picture, however, is by no means complete, nor are all the mechanics explained. The work of the present contract year and the results obtained can best be described under the following topic headings: Proton Energy Effects, Observation of Blisters, Pitting vs Blistering, Oxide Stripping Studies, Crystal Orientation Effects and Irradiation of Gold.

### A. Proton Energy Effects

At energies of about 10 to 50 Kev, protons cause sputtering and removal of the oxide layer on the high purity aluminum. In the range 50 to 70 Kev, blistering occurs spontaneously upon irradiation. At 100 Kev, blistering occurs only after annealing at a temperature of at least 250°C, and the distribution of blisters is sensitive to the substructure of the aluminum[3]. At 200 Kev, blistering has been observed in some instances after annealing, but in other cases no blistering occurred.

These observations are considered typical; specific results will be greatly influenced by the purity and defect structure of the material. For example, 6061 alloy will blister readily upon annealing after irradiation at 200 Kev, and the size of the blisters is quite large compared to those observed on high purity aluminum. Also, cold working markedly influences the size and distribution of blisters obtained[3].

The influence of proton energy on blister formation must be explained on the basis of particle penetration in the aluminum lattice, although data on proton penetrations in these energy ranges are meager. Penetration data in the literature are presented in the form of range energy curves by Young for 1 to 25 Kev protons in aluminum[12], and as energy loss versus proton energy for 50 to 400 Kev protons by Warshaw[13]. Wilcox has converted proton stopping power data into range-energy curves in the range 0 to 350 Kev for aluminum and gold[14]. These reported results indicate an expected penetration of approximately 0.1 to 1.5 microns for protons in the 10 to 200 Kev range.

The reasonableness of some of the conclusions of this present study can be evaluated from a critical analysis of the work of

Ells and Evans with 7 Mev protons[1]. They reported that samples irradiated at temperatures less than 100°C exhibited fine agglomerates, pockets of hydrogen, in the as-irradiated condition. The protons penetrated the aluminum to a depth of about 0.033 cm and the agglomerates were evident upon etching cross-sections of the specimen perpendicular to the irradiated plane. The intragranular agglomerates rarely had radii less than 0.5 micron and most were greater than 1.0 micron. Annealing at 300°C for one hour produced a general coarsening of the agglomerates within the main hydrogen-containing layer and some dispersal of agglomerates at the edges of this layer and in grain boundaries in locations outside the main layer.

The initial width of the hydrogen-containing layer for the 7 Mev protons was estimated to be 0.004 cm (40 microns). The integrated fluxes were of the order of $0.01 \times 10^{17}$ protons/cm$^2$. Assuming a uniform distribution of protons within the layer, the hydrogen content was 0.16 to 22 ppm by weight.

An analysis, similar to that above, indicates that for the present work the hydrogen concentrations could be of the order of 1000 ppm or more. The calculation assumes an integrated flux of $10^{17}$ protons/cm$^2$ and a hydrogen containing layer 0.1 to 0.5 micron thick at mean depths of 0.1 to 1.5 microns below the surface.

Since Ells and Evans report fine agglomerates in as-irradiated samples containing 16 ppm hydrogen in the hydrogen containing layer, it is expected that our samples with a higher concentration of hydrogen near the surface would show similar voids. But these agglomerates may appear as blisters, since their size at low energies is of the order of the penetration depth. At 100 Kev the hydrogen containing layer is apparently too keep to cause spontaneous blistering. Annealing will produce blistering because of agglomerate growth and dispersal, and the distribution of blisters will be sensitive to the substructure because of the favorable sites for nucleation that the subgrain boundaries provide.

The lack of blistering in some samples of high purity aluminum irradiated with 200 Kev protons could be due to the gradual solution of hydrogen in aluminum during annealing before agglomerates are able to coarsen and disperse to a degree that

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affects the surface. Hydrogen will start leaving the penetration produced layer by normal lattice diffusion processes at a significant rate above 300°C so that the agglomerates will contract rather than grow and will eventually disappear[15]. The occurrence of blistering, or lack therof, would be expected to be quite sensitive to microstructure.

Blistering appears to be a consequence of agglomeration of hydrogen just under the surface of aluminum. The hydrogen is introduced into the metal in the form of high energy protons which penetrate the lattice. Agglomeration consists of condensation of hydrogen in the form of the gas into voids or other favorable sites within the metal. The pressure of hydrogen trapped in this manner can cause localized swelling of the metal which is observed as surface blisters.

Results of oxide removal studies, to be discussed under a separate heading, strongly suggest that the blister process is as described above rather than the mere lifting of the oxide surface layer by pockets of hydrogen gas trapped between the metal substrate and the oxide film.

## B. Observation of Blisters

The results reported thus far on the blistering of aluminum surfaces have been based primarily upon observations under the optical microscope under normal incident light. This technique is adequate where the blister size is large enough, but the limit of resolution of the optical microscope is approached for the small blisters formed in high purity aluminum. An electron micrograph of a replica obtained from an aluminum sample irradiated at 100 Kev is shown in Figure 1.

Normal replication techniques yield replicas of the surface of the oxide layer. Techniques are being developed for increasing the thickness of the oxide layer and then removing the oxide as a self-supporting replica[16]. These replicas are expected to provide information both on the structure of the oxide and the surface at the metal-metal oxide interface.

A cellular substructure has been detected in the oxide. The cell size is similar to the size of the blisters formed after proton irradiation, but no direct correlation between oxide cell size and blister size has been established. Examples of the cellular structure can be seen in Figure 2.

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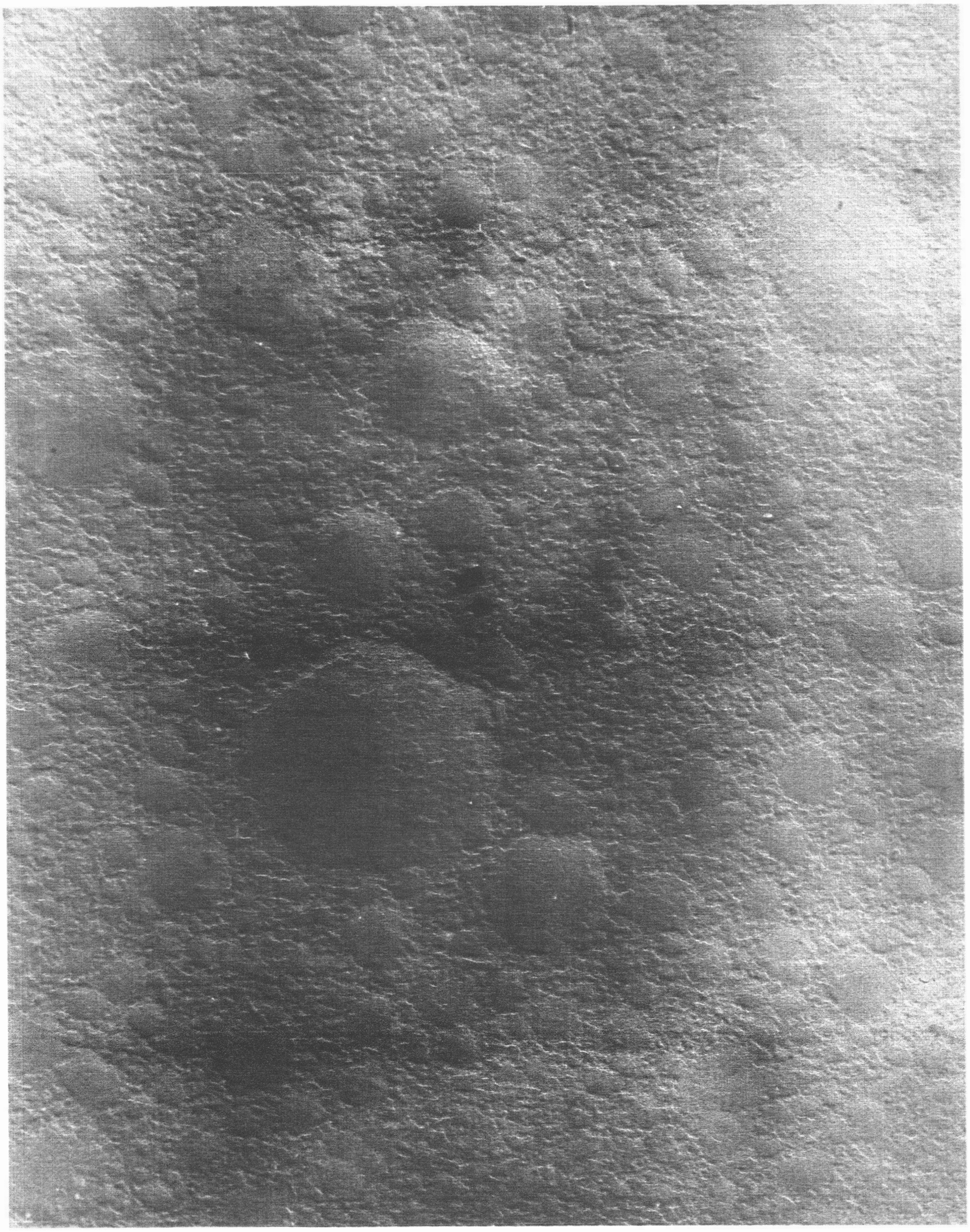


Figure 1 -- Electron Photomicrograph of Blistered Aluminum

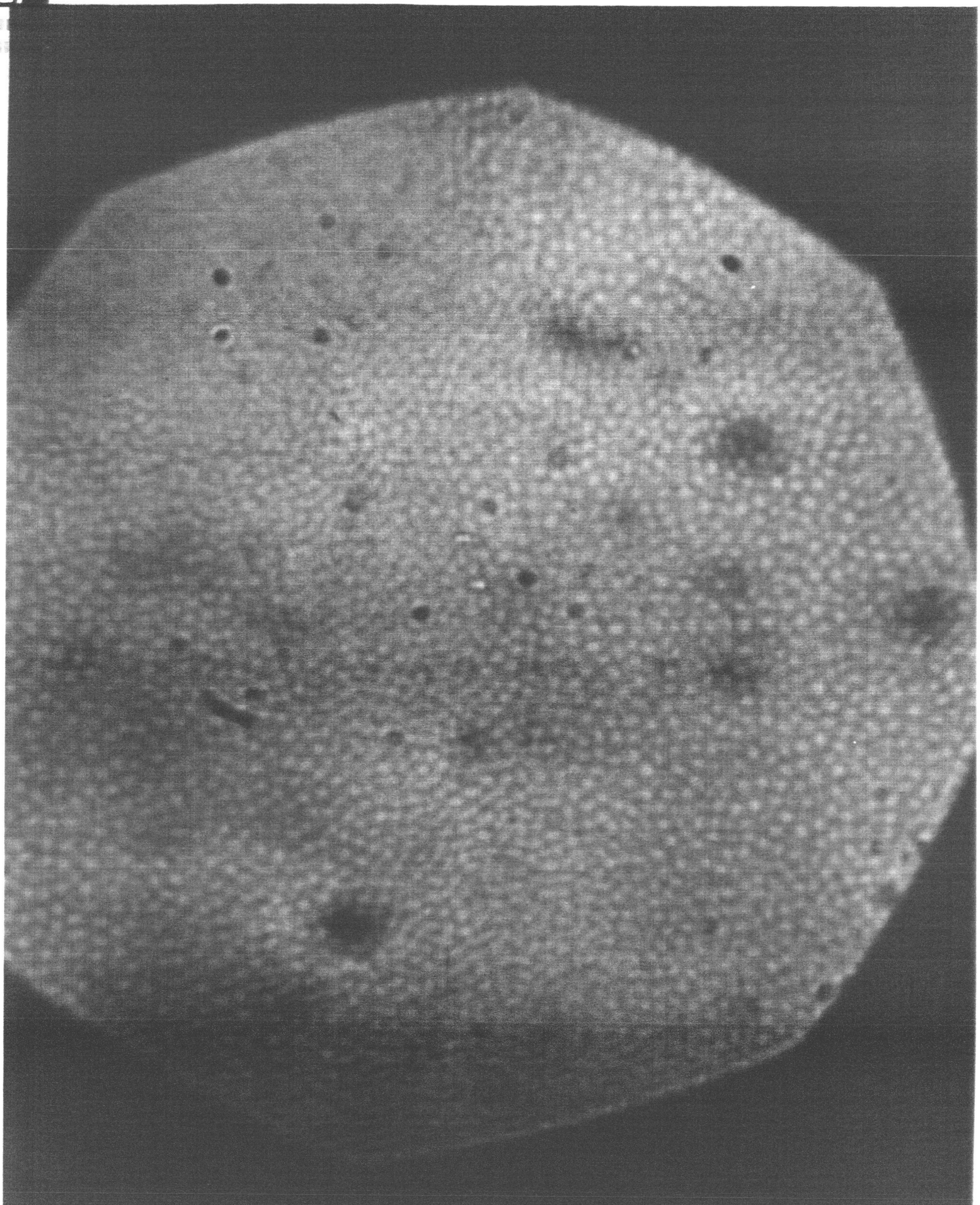


Figure 2 -- Cellular Substructure in Aluminum Oxide

A number of investigators have studied the development of cellular substructures in aluminum oxide[17, 18]. Apparently, the structure is sensitive to the manner in which the film is formed. There may be a relationship between the substructure of the oxide and that of the base material.

Oblique illumination has been found to provide a more sensitive means for detecting the effects of irradiation under the optical microscope than normal incident light. The irradiated areas are sites for diffused scattering of light and appear brighter under the microscope than unirradiated areas which reflect in a normal fashion. The application of oblique illumination is indicated in Figure 3, where the irradiated area is clearly visible at relatively low magnification because of diffuse reflection. Higher magnification is necessary under normal illumination to distinguish pits or blisters, Figure 4.

C. Pitting vs. Blistering

Detailed observation of irradiated surfaces under both normal and oblique illumination indicates that sites for diffuse reflection are not always blisters. Diffuse reflection occurs on samples bombarded with protons of all energies studied within the range 10 to 200 Kev.

At the lower energies, 10 to 50 Kev, much of the diffuse scattering can be attributed to the presence of pitting of the as-irradiated samples. This is considered a sputtering effect. At higher energies, 100 to 200 Kev, some very fine pitting also occurs, but the extensive diffuse scattering observed is attributed to blistering which develops during annealing.

One series of large-grained polycrystalline samples irradiated at 100 Kev was examined on a grain-by-grain basis for substructure, as-irradiated surface damage, and for effects produced by annealing. These samples, although not exhibiting blisters in the as-irradiated condition, did exhibit some small amounts of pitting. Diffuse scattering ascribed to the presence of pits was noted over the entire irradiated area. One sample was subjected to a series of short-time anneals at 300°C. Annealing for 180 seconds produced an increase in diffuse scattering; up to 360 seconds diffuse scattering increased

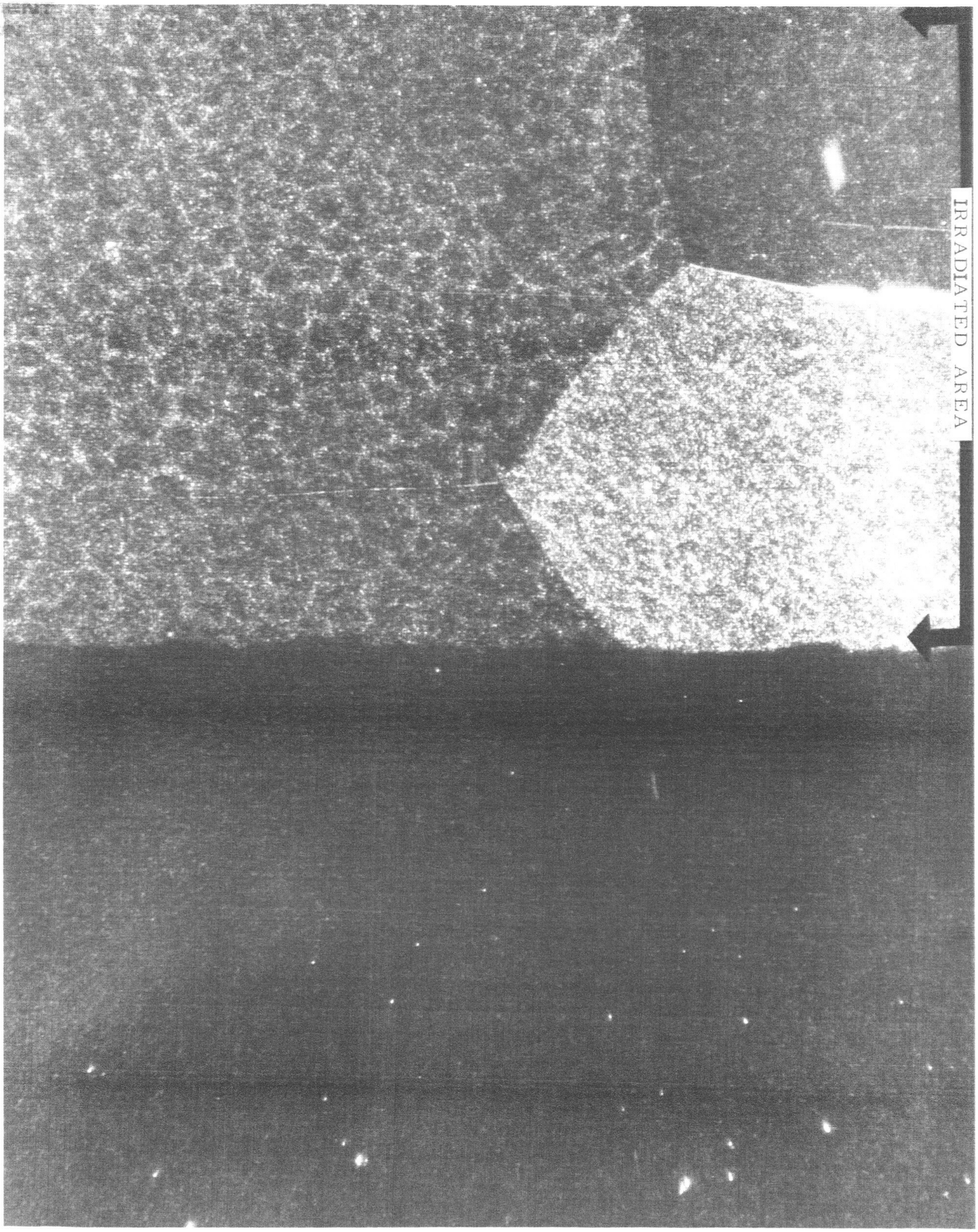



Figure 3 -- Oblique Illumination of Irradiated and Annealed Aluminum

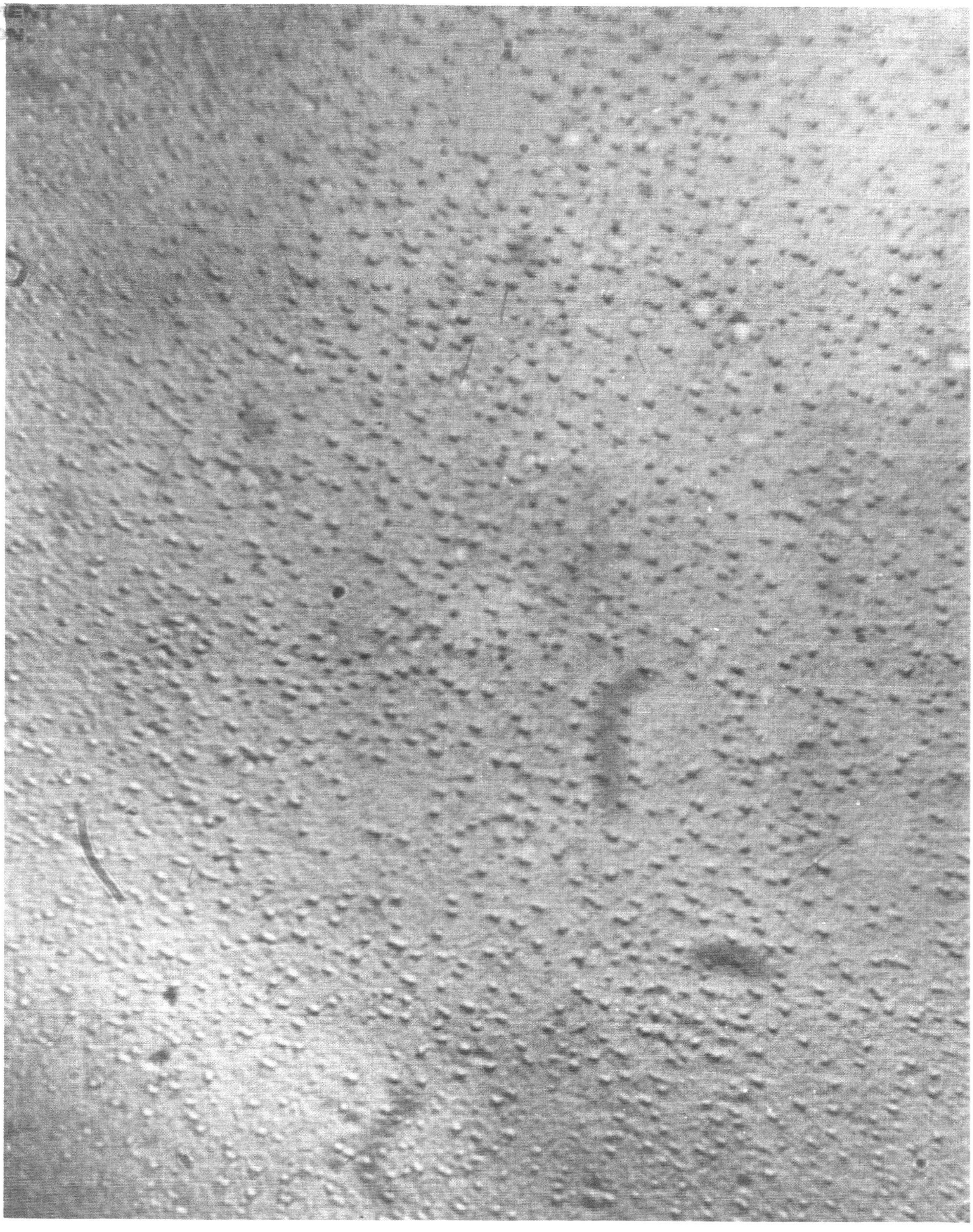


Figure 4 -- Normal Illumination of Irradiated and Annealed Aluminum

and visible blistering occurred; blistering increased for annealing to 500 seconds; additional annealing produced no change.

D. Oxide Stripping Studies

The technique of Lewis and Plumb[21] for chemically stripping the oxide film from a sample without attacking the base material has been used to determine if blisters present after annealing of proton bombarded aluminum are confined to the oxide layer or represent a swelling of the base material. In samples irradiated at 100 Kev and annealed to produce blistering, chemical stripping of the oxide produced no change in the appearance of the blistering, but the pits produced in the as-irradiated condition were eliminated.

The stripping of the oxide did not eliminate the diffuse scattering observed under oblique illumination and attributed to blisters. The same sample was annealed at 600°C for ten hours to produce a thick oxide. Chemical stripping of this new oxide produced no visible change in blistering or in the diffuse scattering resulting therefrom.

These results support the concept that blistering is associated with swelling of the base material and is not merely an effect resulting from trapping of hydrogen under the oxide surface film.

E. Crystal Orientation Effects

An aluminum surface in the as-irradiated condition appears darker than an unirradiated area when examined with the naked eye. Examination of as-irradiated surfaces utilizing the microscope with oblique illumination reveals a diffuse scattering of light from the irradiated area as noted above. This diffuse scattered light originates from many individual sources on the irradiated surface. Microscopic examination under normal illumination reveals these sites to be tiny pits in the irradiated surface.

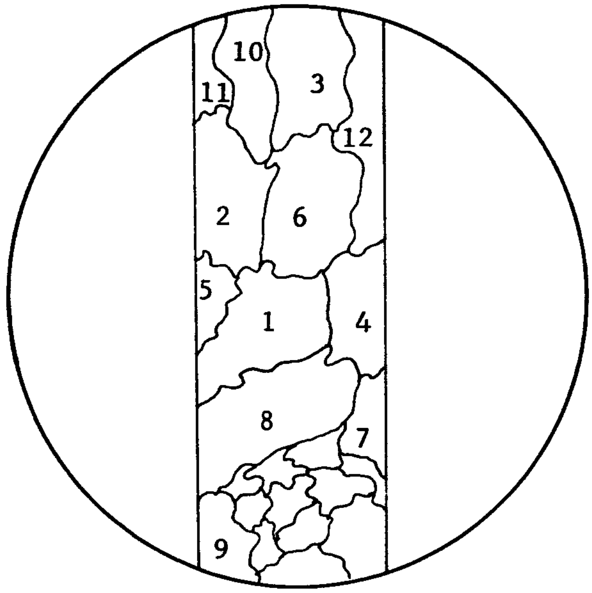
These pits are believed to be due to a removal of the oxide by the impinging ions. This oxide removal is not uniform over the irradiated area, but is rather selectively localized in the form of pits which vary from 0.5 to 5 microns in size.

Examination under the microscope of irradiated specimens from which the oxide had been chemically removed revealed no visible evidence of pitting. This observation indicates that the pitting is localized within the oxide and does not involve removal of the underlying metal.

Examination of irradiated polycrystalline specimens showed that the density of pits per unit area varies among grains as indicated in Figure 5. To correlate this variation in density with crystallographic orientation the Laue back-reflection X-ray technique was utilized to orient approximately 80 crystals on eight specimens. The 80 crystals included all of the grains in the irradiated areas which were equal to or larger than 1 mm in diameter. This lower limit on grain size was imposed by the capability of positioning an individual grain in the path of a microfocus X-ray beam.

The analysis of the variation in pit density among the grains was performed by visual examination utilizing the optical microscope. Both oblique illumination at low magnification, as indicated in Figure 6, and normal illumination at high magnification, Figure 7, were used in this analysis. The oblique illumination method provided striking contrast among the grains for the diffuse scattering of light. Since each pit present on the surface acts as a source for the diffuse scattering of light, the grains with the highest density of pits appear light colored, while the unirradiated area and the grains with a low pit density appear darker. The normal illumination method allows direct viewing of the pits in the range of 1000 to 1500X magnification.

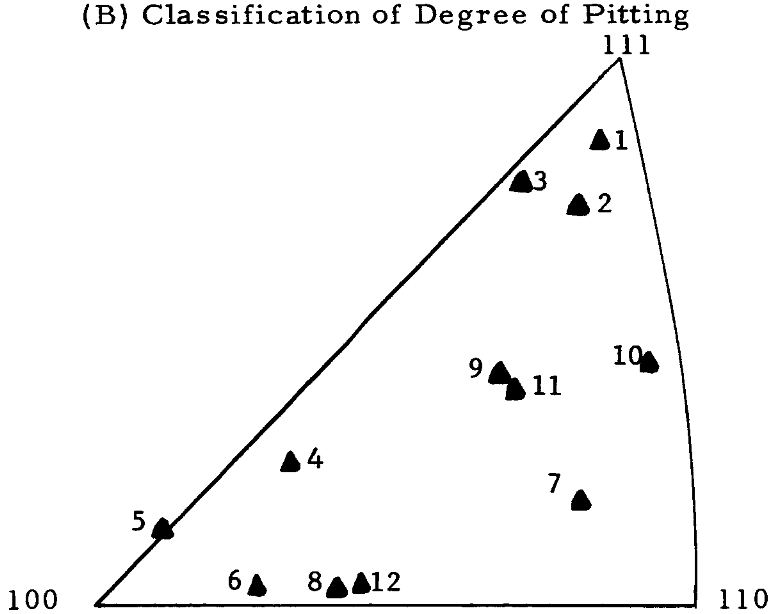
Six specimens used in this study were produced by swaging bulk aluminum to 0.375 in. diameter rod and annealing for approximately two hours at 1100$^{\circ}$F to recrystallize and produce the desired grain size. The crystallographic orientation of the grains showed a preferred orientation near the (100) and (111) poles and an exclusion of the orientations near the (110) pole. To produce crystallographic orientations near the (110) pole, two additional specimens were cut from a 0.5 in. diameter rod which had been pulled in tension until the diameter was reduced to 0.375 in. and annealed at 1100$^{\circ}$F for approximately two hours to recrystallize and produce the desired grain size. The samples were mechanically polished and electropolished prior to irradiation. The proton energies used in these eight specimens were 10, 50, 70, and 100 Kev, with accumulated fluxes of $10^{17}$ p/cm$^2$.




(A) Representation of Irradiated Grains

| HEAVY | MEDIUM | LIGHT |
|---|---|---|
| 4 | 5 | 1 |
| 6 | 9 | 2 |
| 7 | 10 | 3 |
| 8 | 11 | |

(B) Classification of Degree of Pitting




(C) Grain Orientations Plotted on Stereographic Triangle

Figure 5 -- Identification, Classification and Orientation of Grains within Irradiated Region. Classification is based upon degree of pitting.

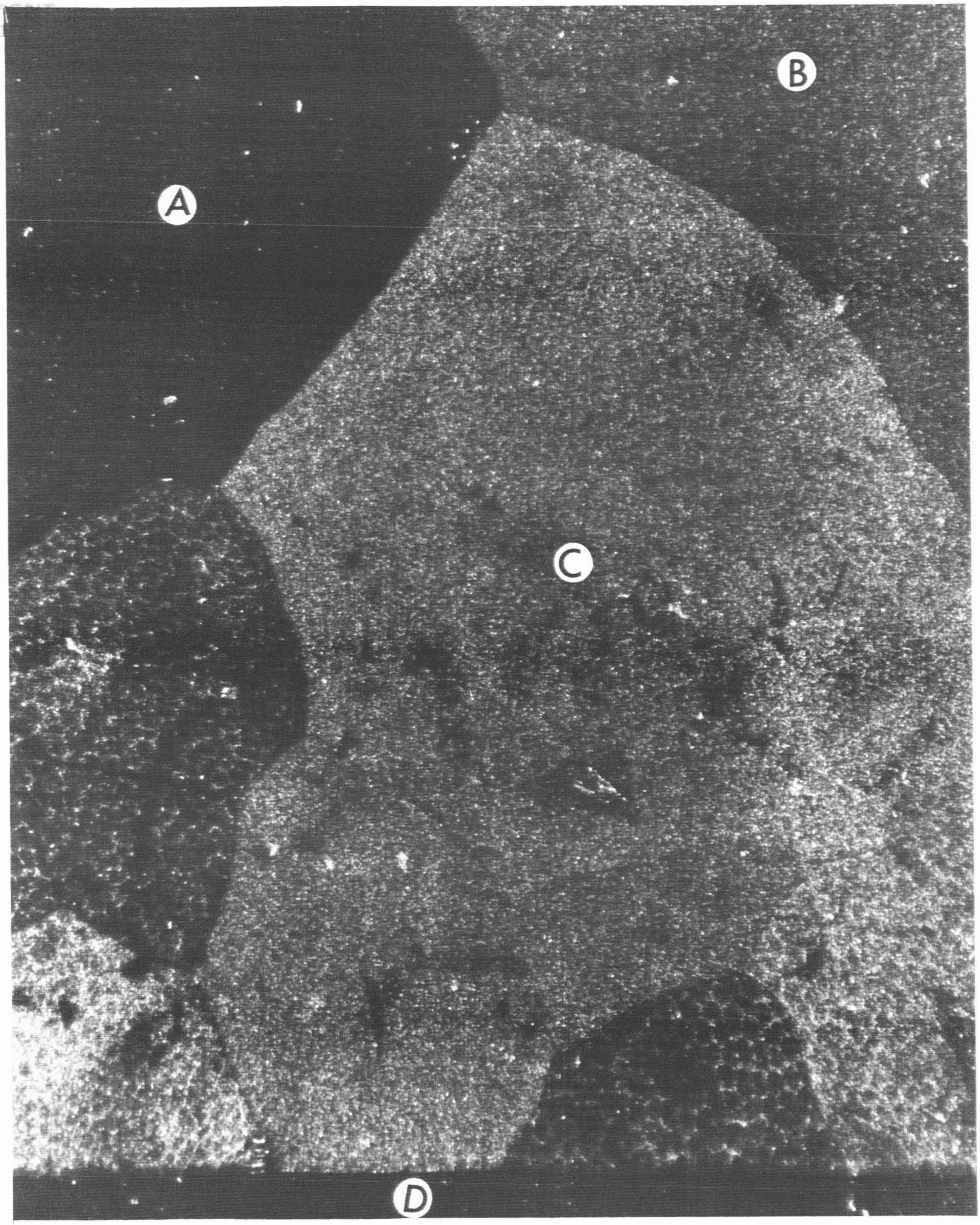



Figure 6 -- As Irradiated Polycrystalline Aluminum Under Oblique Illumination

Figure 7 -- As Irradiated Polycrystalline Aluminum Under Normal Illumination

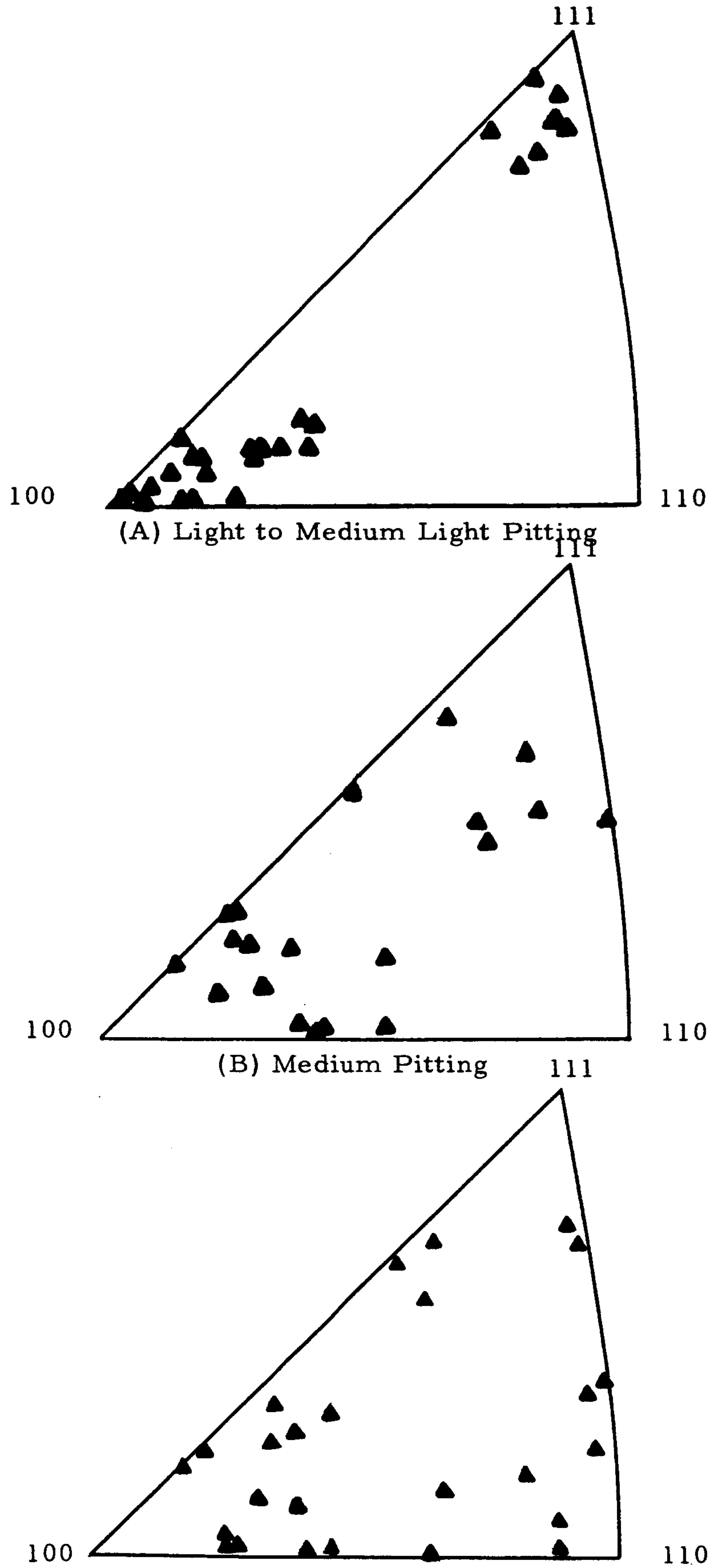
Examination of the pitting at high magnification showed the distribution to be random within a grain with a tendency for an exclusion of pits in the grain boundary region. Examination with oblique illumination at low magnification showed the distribution of pits to be preferentially located along sub-grain boundaries within the grains. This substructure is not readily evident in all specimens or in all grains. There are an insufficient number of pits on some grains to delineate the boundaries and an excessive number of pits on other grains which tend to obliterate any evidence of the boundaries.

A low density of pits was found to be associated with orientations near the (100) and (111) poles. Orientations slightly more removed from these poles possess a moderate density of pits, and orientations in the remainder of the stereographic triangle possess a high density of pits as shown in Figures 8 and 9. This correlation of pit density with orientation may be explained by the possibility of channeling of the impinging protons into the metal lattice along the [100] and [111] directions. It is expected that channeled ions which penetrate deeper into the lattice are less likely to interact with the surface atoms and are, therefore, less likely to cause sputtering. Piercy, and collaborators[20] reported a channeling of heavy ions in aluminum along [100] and [111] directions, but their study showed this effect to also occur for the [110] and [112] directions.

## F. Irradiation of Gold

Experiments to determine the effects of proton bombardment on gold are thus far inconclusive. Six bulk samples of 99.999% purity have been irradiated and two samples which consisted of vapor deposited gold films on aluminum substrates have been irradiated. Four of the bulk samples were mechanically polished and the remainder electropolished. One of the electropolished samples, irradiated at 100 Kev, showed no apparent damage, even after annealing. There was no evidence of blistering on the mechanically polished samples. The proton energies were 10, 40, 70, and 100 Kev.

Both samples with vapor deposited gold films blistered spontaneously. The film thicknesses were 2 microns and the proton energies 10 and 30 Kev. The appearance of the blisters, Figure 10, suggests that the proton penetrated the vapor deposited gold film and that pockets of hydrogen which formed separated the film from the substrate.




(A) Light to Medium Light Pitting

(B) Medium Pitting

(C) Medium-Heavy to Heavy Pitting

Figure 8 -- Orientation of Grains Based Upon Classification According to Degree of Pitting.

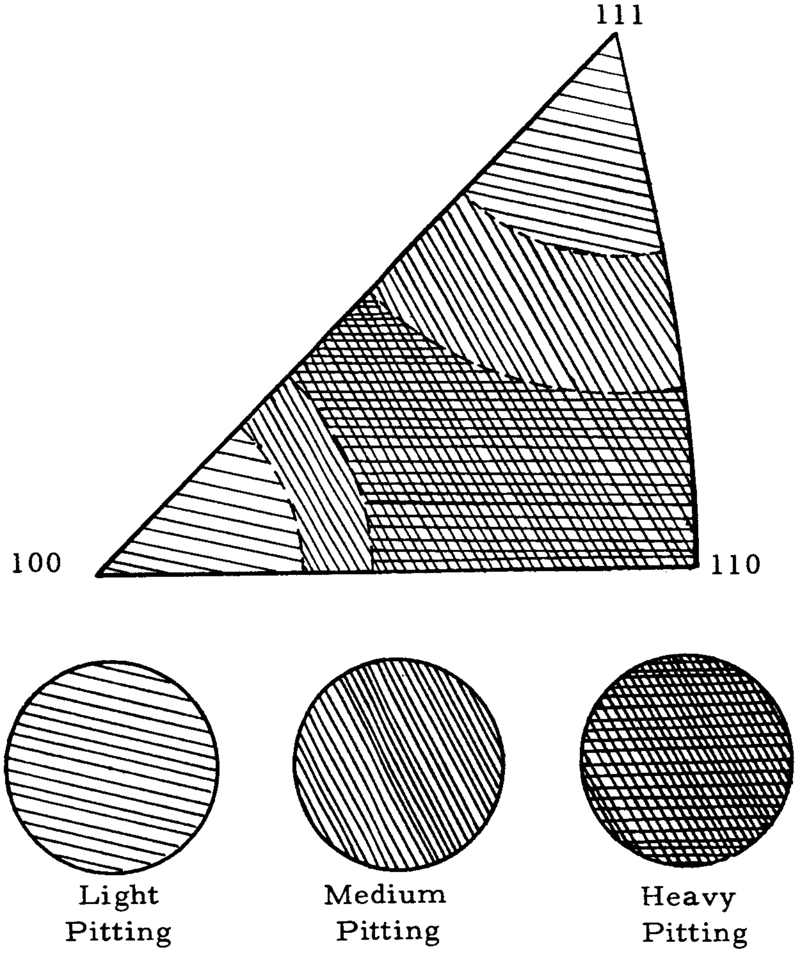



Figure 9 -- Composite Diagram Showing Orientations of Light, Medium, and Heavy Pitting Represented as Areas on Stereographic Triangle.

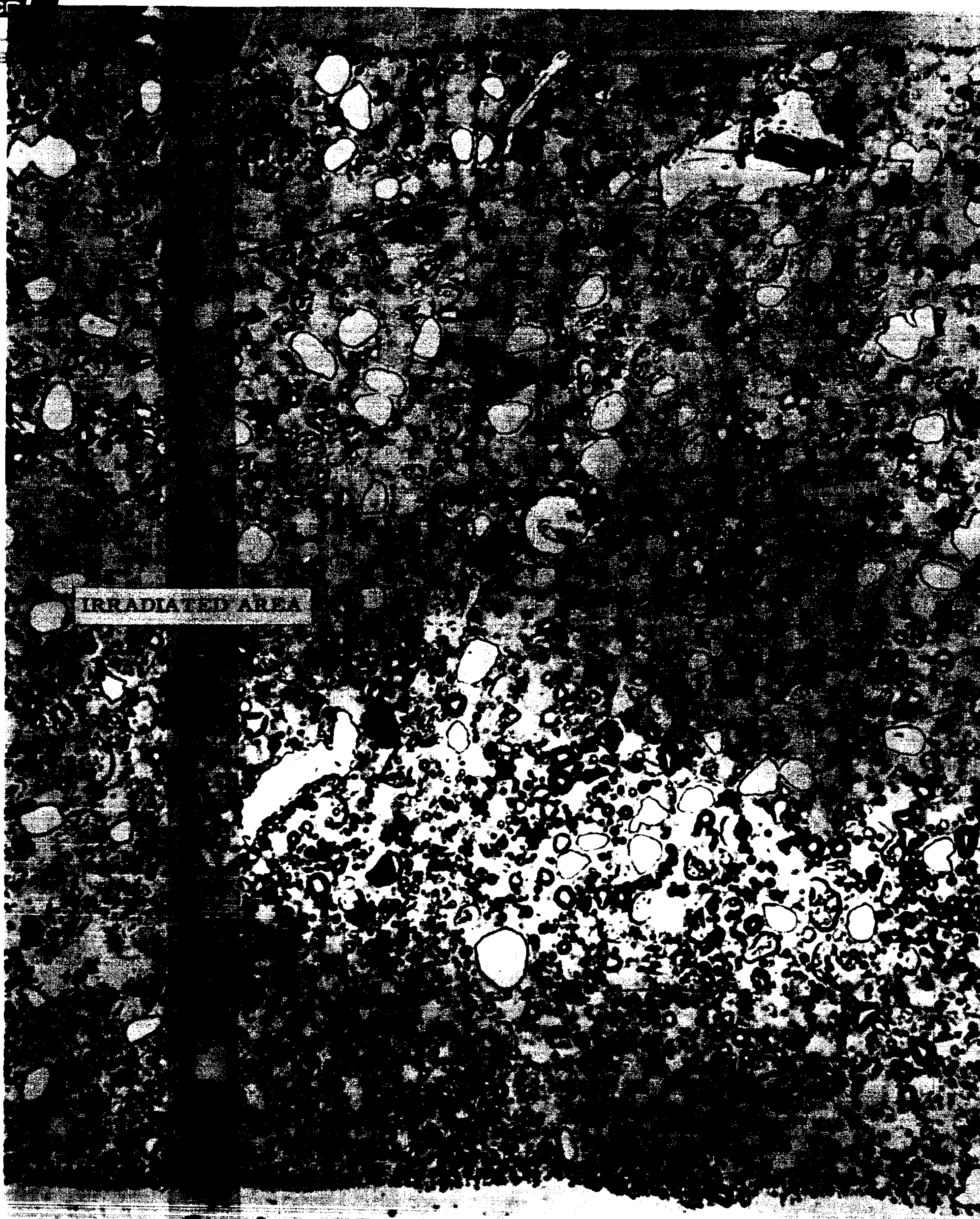



Figure 10 -- Vapor Deposited Au on Al After Irradiation with 10 Kev Protons

## V. SUMMARY AND CONCLUSIONS

Investigation of the effects of proton bombardment of the surface of bulk aluminum in the energy range 7 to 200 Kev reveals that the protons can cause pitting and blistering. Pitting occurs during irradiation and is a manifestation of sputtering. Blistering generally occurs after annealing an irradiated sample and is a result of agglomeration of hydrogen trapped as protons in the metal. The condensation of hydrogen into pockets causes swelling of the metal and surface eruptions likened to blisters. Stripping of the oxide film will eliminate evidences of pitting, but not of blistering.

The relative amounts of pitting and blistering observed are a function of proton energy. At low energies only pitting occurs. As the energy is increased to 200 Kev the amount of pitting decreases and the tendency for blister formation is increased.

The size and distribution of pits and blisters observed is sensitive to metal purity, and microstructure. The distribution of blisters is quite sensitive to subgrain structure in single crystals. Pitting density varies markedly with crystallographic orientation of surface grains and may also be sensitive to subgrain structure.

Blistering of a type analogous to that observed on aluminum has not been detected in bulk gold. Blistering is observed on proton irradiated samples consisting of a gold film evaporated on an aluminum substrate. This latter effect is attributed to trapping of hydrogen between the film and the substrate.

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## VII. APPENDIX

Tabulated below are the sample irradiations conducted under Contract NASw-1203. Sample numbers are a continuation from the preceding year's work under Contract NASw-920. All samples listed here were maintained at 15°C during irradiation.

| Sample No. | Sample Material | Protons Kev | $p/cm^2/sec \times 10^{-12}$ | $p/cm^2 \times 10^{-17}$ |
|---|---|---|---|---|
| 26 | Pure Al | 50 | 2.0 | 0.1 |
| 27 | Pure Al | 50 | 11.0 | 1.0 |
| 28 | Pure Al | 50 | 11.0 | 2.0 |
| 29 | Pure Al | 50 | 11.0 | 0.5 |
| 30 | Pure Al | 50 | 11.0 | 1.0 |
| 31 | Pure Al | 50 | 5.5 | 1.0 |
| 32 | Pure Al | 30 | 11.0 | 1.0 |
| 33 | Pure Al | 70 | 11.0 | 1.0 |
| 34 | Pure Au | 15 | 1.6 | 1.0 |
| 35 | Pure Au | 100 | 6.0 | 1.0 |
| 36 | Pure Au | 40 | 11.0 | 1.0 |
| 37 | Pure Au | 10 | 1.5 | 1.0 |
| 38 | Pure Au | 70 | 11.0 | 1.0 |
| 39 | Pure Au | 100 | 11.0 | 1.0 |
| 40 | Al, Au Plated | 30 | 11.0 | 1.0 |
| 41 | Al, Au Plated | 10 | 1.5 | 1.0 |
| 42 | Pure Al | 7 | 1.5 | 0.5 |
| 43 | Pure Al | 10 | 1.5 | 0.5 |
| 44 | Pure Al | 50 | 11.0 | 1.0 |
| 45 | Pure Al | 100 | 11.0 | 1.0 |
| 46 | Pure Al | 200 | 11.0 | 1.0 |
| 47 | Pure Al | 450 | 5.5 | 0.5 |
| 48 | Pure Al | 100 | 11.0 | 1.0 |
| 49 | Pure Al | 100 | 11.0 | 1.0 |
| 50 | Pure Al | 100 | 11.0 | 1.0 |
| 51 | Pure Al | 100 | 11.0 | 1.0 |
| 52 | Pure Al | 10 | 6.5 | 1.0 |
| 53 | Pure Al | 10 | 6.5 | 0.5 |
| 54 | Pure Al | 10 | 10.0 | 1.0 |
| 55 | Pure Al | 10 | 8.2 | 1.0 |
| 56 | Pure Al | 70 | 8.2 | 1.0 |
| 57 | Pure Al | 100 | 10.0 | 1.0 |
| 58 | Pure Al | 10 | 6.6 | 0.5 |
| 59 | Pure Al | 100 | 10.0 | 1.0 |
| 60 | Pure Al | 10 | 6.6 | 0.5 |

| Sample No. | Sample Material | Protons Kev | p/cm$^2$/sec x $10^{-12}$ | p/cm$^2$ x $10^{-17}$ |
|---|---|---|---|---|
| 61 | Pure Al | 50 | 8.0 | 1.0 |
| 62 | Pure Al | 50 | 8.0 | 1.0 |
| 63 | Pure Al | 100 | 8.0 | 1.0 |
| 64 | Pure Al | 100 | 6.6 | 1.0 |
| 65 | Pure Al | 70 | 11.0 | 1.0 |
| 66 | Pure Al | 70 | 8.0 | 1.0 |
| 67 | Pure Al | 100 | 10.0 | 1.0 |
| 68 | Pure Al | 100 | 8.0 | 1.0 |
| 69 | Pure Al | 100 | 8.0 | 1.0 |
| 70 | Pure Al | 100 | 10.0 | 1.0 |
| 71 | Pure Al | 100 | 11.0 | 1.0 |
| 72 | Pure Al | 100 | 8.0 | 1.0 |
| 73 | Pure Al | 100 | 10.0 | 1.0 |
| 74 | Pure Al | 100 | 8.0 | 1.0 |
| 75 | Pure Al | 100 | 10.0 | 1.0 |
| 76 | Pure Al | 100 | 8.0 | 1.0 |
| 77 | Pure Al | 100 | 10.0 | 1.0 |
| 78 | Pure Al | 100 | 10.0 | 1.0 |
| 79 | Pure Al | 100 | 10.0 | 1.0 |
| 80 | Pure Al | 100 | 10.0 | 1.0 |